



Short communication

Modification of Nafion membrane by Pd-impregnation via electric field

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H I G H L I G H T S

- Pd–Nafion membrane was prepared by an improved impregnation–reduction method.
- Electric field was used to enhance the movement of Pd ion toward Nafion membrane.
- Methanol crossover of Nafion membrane was lowered by the improved modification method.

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This paper presents an improved impregnation–reduction (I–R) method for modifying a Nafion membrane that achieves a lower methanol crossover. During impregnation of the Nafion membrane in $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ solution, an electric field was conducted across the membrane to enhance the migration of Pd ions. After impregnation, Pd ions were reduced to form Pd nanoparticles by soaking the membrane in NaBH_4 solution. The test results show that the Pd–Nafion membrane prepared by the improved I–R method has higher proton conductivity and lower methanol permeability than that prepared by usual I–R method.

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1. Introduction

Direct methanol fuel cells (DMFC) have numerous advantages over other energy storage systems: a low operating temperature (below 100 °C), a fast response to dynamic loads, and a high theoretical energy density (6100 Wh kg^{-1} based on fuel weight). As a result, DMFCs have attracted considerable attention as a replacement for batteries in portable devices such as music systems and cellular telephones [1,2]. One of the challenges restraining the commercial application of DMFCs is methanol crossover from the anode to the cathode side through the proton exchange membrane (typically a Nafion series membrane) [3]. The crossed methanol not only results in fuel loss, but also leads to a mixed potential at the cathode due to a direct methanol oxidation reaction on the cathode platinum catalyst. This reduction severely reduces the electrode potential, which therefore reduces the overall cell voltage. To

overcome this disadvantage, extensive work has been conducted on polymer membrane modification and development [3–5].

Based on an ideal cluster–network model, a Nafion membrane can be characterized as a microphase-separated structure composed of a hydrophobic fluorocarbon phase and hydrophilic SO_3^- end groups, where methanol crossover occurs through the channels produced by this microphase separation [6,7]. Palladium (Pd) has proven to be theoretically impermeable to methanol, but shows sufficient permeability to hydrogen and is therefore often used to modify commercially available Nafion membranes to reduce methanol crossover [8–12]. Among these modification techniques, the impregnation–reduction method (I–R method) can introduce Pd particles smaller than 30 nm into the Nafion membrane to block methanol permeability [6,13–16]. Previous studies have shown that a Pd-impregnated Nafion membrane (Pd–Nafion membrane) significantly reduces methanol crossover, particularly at high methanol concentrations, without affecting the proton conductivity of the membrane [14–16].

In this work, we present an improved I–R method to prepare a Pd–Nafion membrane. During impregnation of the Nafion membrane in a $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ solution, an electric field was

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conducted across the Nafion membrane to enhance migration of the $\text{Pd}(\text{NH}_3)_4^{2+}$ ions. To reduce Pd^{2+} , the membrane was dipped into a NaBH_4 solution to form Pd nanoparticles. The proton conductivity and methanol crossover of the prepared Pd–Nafion membrane was then examined, and a micro DMFC constructed with a Pd–Nafion membrane was tested to study the membrane's performance.

2. Experiment

Prior to impregnation, Nafion 117 membranes were pretreated to remove dirt, organic impurities, and inorganic metal ions by successively soaking the membranes at 80 °C for an hour in the following solutions: 3% H_2O_2 , deionized water, 0.5M H_2SO_4 , and finally deionized water. Pd-impregnated Nafion (Pd–Nafion) membranes were prepared in electrolytic cell, as shown in Fig. 1a, where two Pt plate electrodes were placed on both sides of the Nafion membrane. The chambers were filled with a solution of 0.01 M $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ fixed at a pH of 11.5. During an impregnation period lasting 1 h, the impulse electric signal shown in Fig. 1b was conducted across the Pt plates, forming an electric field to enhance the migration of $\text{Pd}(\text{NH}_3)_4^{2+}$ ions into the Nafion membrane. After impregnation, the membranes were washed with deionized water several times and then treated again by soaking the membranes in successive order with a 0.01 M NaBH_4 solution at 40 °C for 2 h, a 0.5 M H_2SO_4 solution at 80 °C for an hour, and deionized water at 80 °C for an hour. Finally, the proton conductivity of the Pd–Nafion membrane was measured using electrochemical impedance spectroscopy (EIS) [17].

Commercial anode and cathode gas diffusion electrodes (purchased from Johnson Matthey, Inc.) with an area of 1 cm² were attached to the Pd–Nafion membrane by hot-pressing at 135 °C and 10 MPa for 180 s to form a membrane electrode assembly (MEA). A Single DMFC was prepared by sandwiching the MEA between two Au-deposited stainless steel plates with open areas of ca. 45% for the anode and cathode. Air was only supplied to the electrodes by diffusion through the open areas. A methanol solution reservoir was built into the anode fixture, allowing methanol to diffuse into the catalyst layer from the built-in reservoir. There was no external pump used in our passive DMFC system. Current–voltage (I–V) polarization curves were obtained at 40 °C and power density was determined from the I–V curves. The methanol permeation rate through the Nafion membrane was also evaluated by linear sweep voltammetry (LSV) with a scan rate of 1 mV s^{−1} [7]. For the LSV measurement, the cathode was supplied with an inert atmosphere of well-humidified nitrogen, and the cathode and anode were served as working and counter/reference electrodes, respectively. All electrochemical measurements were carried out using a CHI 660C electrochemical analyzer (Shanghai, China).

3. Results and discussion

The parameters of the impulse electric signal were determined as following. First, a frequency sweep was performed on the cell from 10⁵ Hz to 10^{−3} Hz with amplitude of ±10 mV, and the results are given in Fig. 2. It can be found that the impedance starts to increase sharply for frequencies lower than 10³ Hz. This increase is due to the strong polarization of the electrochemical reaction occurring at the Pt/solution interfaces. Clearly, the large impedance will lead to a small current flowing through the solution. This means that the voltage drop, i.e., the strength of the electrical field across the Nafion membrane, increases with frequency. In order to obtain a strong electric field, the frequency of the impulse electric signal was set to 10⁴ Hz. At this frequency, it was found that the amplitude of the impulse electric signal (V_p) reaching 4 V not only led to the color change of the $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ solution from colorless to yellow, but also made both Pt plates turn black. At this point, significant changes occurred to the composition of the $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ solution due to the strong electrochemical reactions occurring at the Pt/solution interfaces. Therefore, the V_p value was maintained below 4 V and the frequency at 10⁴ Hz for the remainder of the experiment.

Table 1 gives the proton conductivity of the Pd–Nafion membrane, as measured by EIS. It can be seen that the proton conductivity of the Pd–Nafion membrane is higher than that of the pure Nafion 117 membrane. As the V_p value increases, the proton conductivity of the Pd–Nafion membrane increases. This means the Nafion membrane modified with the improved I–R method has better proton conductivity than membranes modified with the usual I–R method. With the usual I–R method, Pd ions are driven into the ionic cluster network of the Nafion membrane as the result of the concentration difference between the Pd ions in the bulk solution region and inside the membrane. An electric signal applied across the Nafion membrane, as shown in Fig. 1, can drive more Pd ions into the ionic cluster network of the Nafion membrane via the electric field. After the reduction of Pd ions to Pd atoms, the Nafion membrane modified with the improved I–R method tends to form more and larger Pd particles inside its ionic cluster network, which has been shown to be beneficial for improving the proton conductivity of a Pd–Nafion membrane [14].

Fig. 3 shows the results of linear sweep voltammetry tests used to characterize the Nafion membrane's permeability toward methanol. The methanol permeation rate through the Nafion membrane (j) was determined by measuring the steady-state limiting current density (i_{lim}) resulting from complete electro-oxidation at the Nafion membrane/Pt catalyst interface. The i_{lim} value is the current density at the plateau of the methanol permeation rate-limited region. However, taking into account the

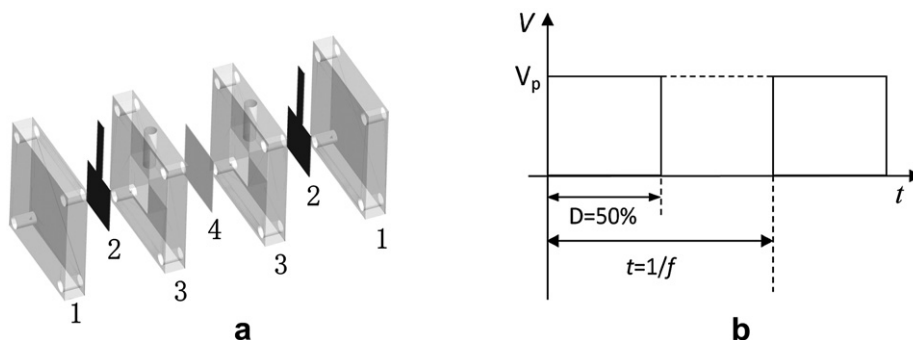


Fig. 1. Electrolytic cell (a) and electric signal (b) used to modify a Nafion membrane with Pd impregnation. 1. End plates; 2. Pt plates; 3. solution reservoir; 4. Nafion membrane.

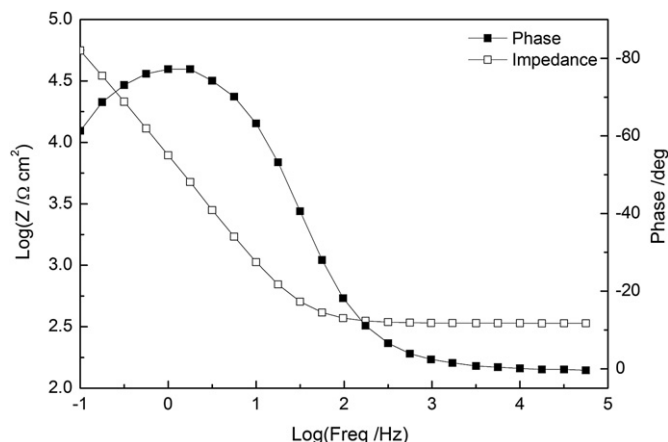


Fig. 2. Bode plot of a Nafion membrane in $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ solution.

effect of electro-osmotic drag on methanol transport in the membrane, the methanol permeation rate should be corrected and written as [7]

$$j = \frac{1}{k_{dl}} \frac{i_{lim}}{6F} \quad (1)$$

where F is Faraday's constant and k_{dl} is the electro-osmotic drag correction factor for i_{lim} . Table 2 lists the corresponding results of i_{lim} and j . The results show that when the anode is fed with 2 M methanol solution, the methanol permeation rate decreases with the increasing V_p value, although this decrease is not greatly affected by the impregnation of Pd particles because methanol crossover is not serious at low methanol concentrations. However, when the methanol concentration is increased to 8 M, methanol crossover becomes much more serious due to the higher methanol concentration, and the pure Nafion membrane has a much larger methanol permeation rate than the Pd–Nafion membrane. This result indicates a greatly reduced methanol crossover for the Pd–Nafion membrane. Compared with the usual I–R method, the improved I–R method causes the modified Nafion membrane to exhibit a smaller methanol permeation rate.

According to the model of an ideal cluster network, methanol crossover arises from transportation of methanol molecules through the hydrophilic cluster inside the Nafion membrane [7]. When Pd particles or nanoparticles fill these clusters, methanol transportation through the Nafion membrane can be restricted without loss of proton conductivity. Using an electric field during impregnation of the Nafion membrane in a $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ solution drives more Pd ions into the clusters, thus causing more and larger Pd particles to form inside the membrane [14]. As a result, a Nafion membrane modified with the improved I–R method exhibits a smaller methanol permeation rate than a membrane modified with the usual I–R method. The Pd particle content inside the Nafion membrane increases as the V_p value increases, causing the decrease in the methanol permeation rate.

Fig. 4 shows the polarization curves and power density outputs of DMFCs with pure Nafion and Pd–Nafion membranes. Because of

Table 1
Proton conductivity of Pd-impregnated Nafion membrane.

Membrane	Nafion117	Pd–Nafion		
		$V_p = 0 \text{ V}$	$V_p = 1 \text{ V}$	$V_p = 3 \text{ V}$
Conductivity/ S cm^{-1}	$1.25\text{E}-2$	$1.32\text{E}-2$	$1.45\text{E}-2$	$1.54\text{E}-2$

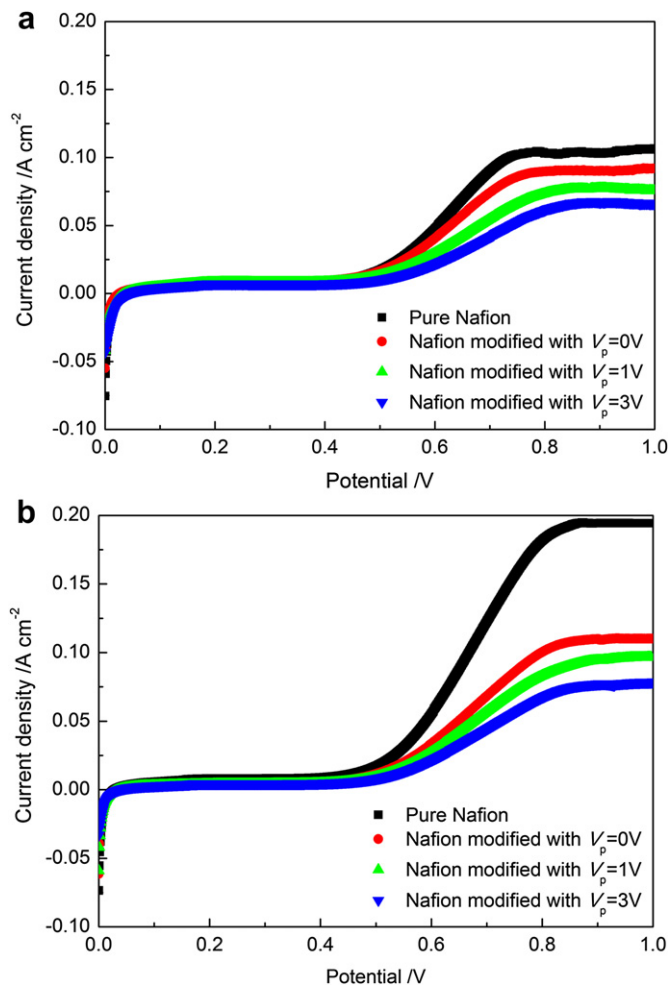


Fig. 3. Voltammetric curves at the methanol concentrations of 2 M (a) and 8 M (b) for the oxidation of methanol permeating through Pd-impregnated Nafion membranes.

higher proton conductivity and smaller methanol crossover, cell performance is better when using a Pd–Nafion membrane. This superiority is further increased by the improved modification method of the Nafion membrane. When the cell is fed with a 2 M methanol solution, the difference in cell performance is not quite obvious because of low methanol crossover. However, when the methanol concentration is increased to 8 M, the performance difference becomes quite significant. Using a pure Nafion membrane, the cell performance declines dramatically by ~40%, from 22 mW cm^{-2} to 13 mW cm^{-2} , due to serious methanol crossover. On the other hand, the cell performance with a Pd–Nafion membrane increases because of the high methanol

Table 2

Limiting current density i_{lim} and methanol permeation rate j of Pd-impregnated Nafion membrane exposed to 2 M and 8 M methanol.

Membrane	Nafion117	Pd–Nafion		
		$V_p = 0 \text{ V}$	$V_p = 1 \text{ V}$	$V_p = 3 \text{ V}$
i_{lim} at 2 M ^a / mA cm^{-2}	104	90	77	67
j at 2 M ^b / $\text{mol cm}^{-2} \text{ s}^{-1}$	$2.25\text{E}-9$	$1.94\text{E}-9$	$1.66\text{E}-9$	$1.45\text{E}-9$
i_{lim} at 8 M ^a / mA cm^{-2}	194	110	95	78
j at 8 M ^b / $\text{mol cm}^{-2} \text{ s}^{-1}$	$6.71\text{E}-9$	$3.79\text{E}-9$	$3.28\text{E}-9$	$2.69\text{E}-9$

^a Limiting methanol crossover current density is obtained from Fig. 3.

^b The k_{dl} value is about 0.8 at methanol concentration of 2 M [7].

^c The k_{dl} value is about 0.5 at methanol concentration of 8 M [7].

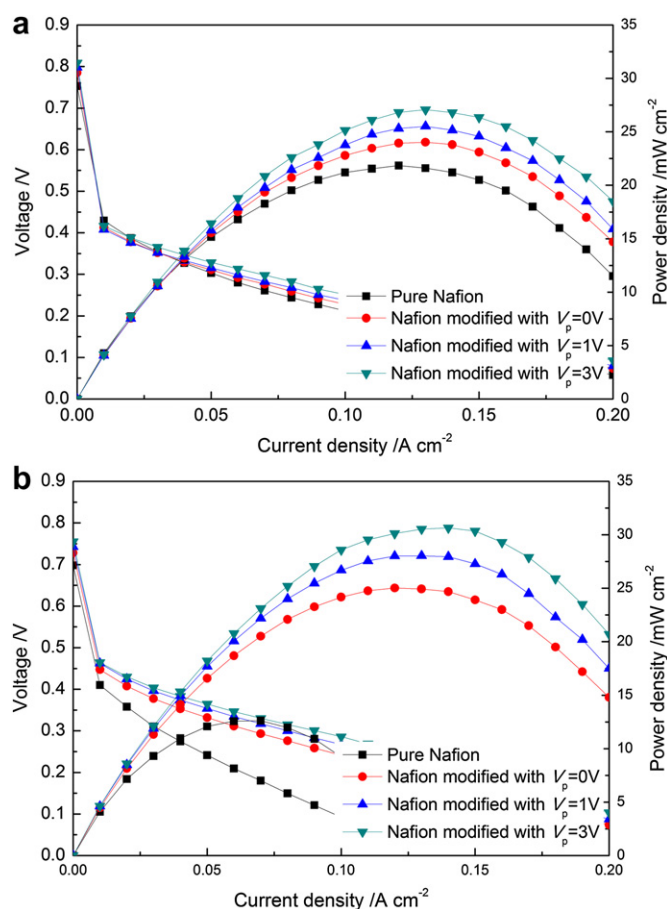


Fig. 4. Polarization curves using 2 M (a) and 8 M (b) methanol solution as fuel for DMFCs fabricated with Pd-impregnated Nafion membranes.

concentration gradient. The cell with a Pd–Nafion membrane prepared using the improved I–R method with $V_p = 3$ V shows a performance increase of 15%, from 27 mW cm^{-2} to 31 mW cm^{-2} , while the cell using the Pd–Nafion membrane prepared with the usual I–R method only shows a performance increase of 4%, from 24 mW cm^{-2} to 25 mW cm^{-2} . These results indicate that a Pd–Nafion membrane prepared using the improved I–R method enables a DMFC to operate at a higher methanol concentration than a cell with a Pd-membrane prepared using the usual I–R method.

4. Conclusions

A Pd–Nafion membrane was prepared using an improved impregnation–reduction (I–R) method, which applies an electric field to enhance the migration of Pd into the Nafion membrane. Compared with the usual I–R method, the new method causes more Pd particles to deposit into the membrane. Our results show that a Pd–Nafion membrane prepared using the improved I–R method has better proton conductivity and smaller methanol permeation rate than membranes prepared with the usual I–R method, enabling a DMFC to operate at a higher methanol concentration. More detailed research work about the improved I–R method is currently being carried out in our lab.

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